

Origin and Underground Flow Time of Thermal Waters in Crystalline Basement Complexes

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Introduction

Thermal springs usually differ from normal groundwater springs in the area where they emerge by their higher temperature and exceptional chemical composition. They issue at temperatures which are often well above the annual average ground temperature in the vicinity and their mineral content ranges from fractions of a gram to several grams per litre.

Most thermal waters owe their high temperatures to the fact that the temperature of the earth rises by an average of 1° C with every 33 metres of overlying rock (geothermal gradient). The heat of the rocks is picked up by infiltrating precipitation which, if the geological conditions are right, finds its way into large fissures along which it rises to the surface with sufficient speed to avoid cooling. Local increases in the ground temperature through magmatic intrusion and exothermal chemical processes (oxidation in pyrites deposits, hydration of anhydrides) favour the existence of warm springs. Heat produced by the decay of radioactive minerals (A. THURNER, 1967) and by biological processes such as the bacterial sulphate reaction may also raise the temperature of vadose waters (K. H. WALLHÄUSER and H. PUCHELT, 1966). There has been considerable discussion of the possibility that thermal springs derive from the condensation of steam given off by magmatic deposits (juvenile water) or from the distillation of water out of hot rock formations (fossil water). However, conclusive evidence in support of these mechanisms has not yet been found, not even in the case of soffioni and fumaroles in recent volcanic regions. The same applies to the view, advocated in particular by I. STINI (1954), that vadose waters are heated by juvenile steam.

In hydrology, as in many other fields, isotope techniques have opened new possibilities for the investigation of such problems. Tritium, the radioactive isotope of hydrogen produced by the interaction of cosmic radiation with the atmosphere is entering the ground, as a heavy molecule of water (HTO) together with infiltrating precipitation. The constant rate of cosmic ray production of tritium has been swamped by the

injection of large pulses of tritium from nuclear detonations in the atmosphere. The presence of tritium in groundwater indicates its recent atmospheric origin and, in some favourable cases, may indicate the groundwater flow time.

The isotopes ^{12}C , ^{13}C and ^{14}C are present in widely differing amounts in the element carbon. The average abundance of the lightest isotope, ^{12}C , is 98.9%, of ^{13}C about 1.1% and of the radioactive isotope ^{14}C , only $10^{-10}\%$.

Plants and bacteria in the soil prefer ^{12}C for building organic compounds, so that carbon dioxide resulting from the decomposition or decay of organic material contains less ^{13}C than carbon dioxide of magmatic origin or the carbonates of non-organogenic limestones. Isotopic ratios are usually given in the form of so-called δ -values. Essentially, the δ value represents the ratio between the isotopic ratio of the sample under consideration and that of a standard sample. Non-organogenic marine limestone, which has a fairly constant $^{13}\text{C}/^{12}\text{C}$ ratio, is used as a standard in the determination of ^{13}C . A sample of any marine limestone thus has a $\delta^{13}\text{C}$ -value near zero when compared with a standard also consisting of marine limestone. Biogenic material also has a more or less constant $^{13}\text{C}/^{12}\text{C}$ ratio, but, due to its relative enrichment in ^{12}C , contains less ^{13}C than marine limestone and usually yields $\delta^{13}\text{C}$ -values of about -25% (E. INGERSON and F. I. PEARSON, 1964; F. I. PEARSON and D. E. WHITE, 1967). The $\delta^{13}\text{C}$ -value of a carbonate sample of mixed (biogenic and mineral) origin lies between zero and -25% , depending on the ratio of biogenic to mineral carbon present.

Biogenic CO_2 , which reaches concentrations of 3.5 vol. % in the air trapped in humus-rich soil and infiltrates with rainwater, releases calcium carbonate from calciferous rocks through chemical attack. When this is a non-recurrent, completed process, a Mol of biogenic CO_2 having a $\delta^{13}\text{C}$ -value of -25% reacts with a Mol of rock carbonate having a $\delta^{13}\text{C}$ -value of zero, the $\delta^{13}\text{C}$ -value of the water-dissolved carbonate lying exactly mid-way between zero and -25% (i. e. at -12.5%). However, the reaction of biogenic CO_2 with rock carbonates is not always a non-recurrent process (R. BRINKMANN, K. O. MÜNNICH and J. C. VOGEL, 1959): the dissolved calcium bicarbonate may be precipitated as a result of evaporation, particularly in arid zones, and subsequently redissolved by water containing a fresh supply of biogenic CO_2 . The abundance of ^{13}C in the dissolved carbonate then increases, the $\delta^{13}\text{C}$ -value moving towards -25% . Other processes may operate in the opposite direction, causing the $\delta^{13}\text{C}$ -value to shift towards zero—for example, the dissolution of rock carbonates in CO_2 -free water (which occurs on a significant scale, however, only when there is a simultaneous exchange of calcium for the sodium from argillaceous minerals) and the intrusion of magmatic CO_2 . In general, $\delta^{13}\text{C}$ -values close to or over -12.5% indicate that the water is of vadose origin.

The radioisotope ^{14}C is formed from the nitrogen (^{14}N) of the air (through cosmic neutron irradiation and—in recent years—through neutron collisions resulting from nuclear bomb explosions in the stratosphere) and combines with the oxygen of the air to form CO_2 . The balance between the production and radioactive decay of ^{14}C determines its concentration in the atmosphere at any given time; compared with the concentration of normal, stable carbon (^{12}C), it is extremely low ($10^{-10}\%$) but measurable due to radioactivity of radiocarbon. Part of the CO_2 in the atmosphere finds its way into the ground with precipitation or through plants. As soon as the exchange with the atmospheric carbon reservoir is interrupted through the infiltration of the CO_2 -rich water to the groundwater system, the ^{14}C content of the carbonates decreases as a result of radioactive decay with a half-life of 5730 years. It is, therefore, possible to determine the time span between the moment rainwater enters the ground and its reappearance as a spring.

The ^{14}C concentration in biogenic material corresponding to the constant rate of cosmic ray production of radiocarbon is referred to as "modern ^{14}C content". The year of reference is 1950. Since 1952, due to thermonuclear detonations, a considerable amount of ^{14}C has been added to the atmospheric reservoir. The present levels of ^{14}C in the atmosphere are thus larger than "modern" by a factor up to two in 1963 (K. O. MÜNNICH and W. ROETHER, 1967).

"Dating" of water is done by determining the ^{14}C concentration in carbonates and bicarbonates extracted from a water sample and comparing this concentration with the standard (e. g. NBS "modern"-standard) corresponding to the ^{14}C atmospheric content in 1950. The ^{14}C method is, in principle, suitable for determining ages ranging from a few hundred to 40 thousand years. Some limitations, however, due to phenomena taking place in the soil and water bearing geological formations must be kept in mind during the interpretation of ^{14}C results. First, the carbon content of biogenic origin in water can vary between 50% and 100% depending upon the presence of carbonate minerals in the soil, during infiltration to the groundwater system. This fact can, in general, be controlled by measuring $\delta^{13}\text{C}$ and applying a proposed correction factor to the measured ^{14}C value. Second, the initial isotopic ratio of carbon may undergo some changes due to a possible exchange of carbon species in water with carbon species in the surrounding rock no longer contain any ^{14}C . If the exchange processes affect both ^{14}C and ^{13}C isotopes in the same way, the $\delta^{13}\text{C}$ correction factor should take it into account. Much attention is now being given to the problem of (especially in elevated temperatures). The latter, because of their age radiocarbon dating of water but no final conclusions have yet been drawn as to the importance of various factors in carbonate isotopes geochemistry. In general, various mentioned and unmentioned disturb-

ing effects cause a dilution of biogenic carbon in water and, thus, the radiocarbon apparent age of water is usually higher than the true age.

Thermal water springs have usually also a cold surface water contribution, the ^{14}C content of which may be at present higher than "modern". Determination of the tritium content is here very helpful for estimating this surface water contribution.

Programme and Method

Carbon dating and tritium studies were performed on water from two thermal springs and a mixed-water spring in Bad Gastein (March 1968) and from four thermal springs in the Pyrenees (July 1968).

The carbon species have been extracted from water samples by precipitation of barium carbonate after making alkaline with sodium hydroxide. The precipitation was done in an funnel-like plastic cylinder, especially designed by I.A.E.A., with a capacity of about 65 litres (Fig. 1). A one-litre plastic bottle is screwed to the bottom of the funnel, in which the precipitate is collected. The precipitate is formed by adding barium chloride to the water. Normally, the precipitate is rather fine and requires several hours to settle so that a coagulating agent (Praestol) is added to promote agglomeration and rapid settling in the bottle. The separation of carbon from water should be complete to avoid isotope fractionation effects. With the method described here, the whole procedure is completed in about 30 minutes. The bottle containing carbonate is then unscrewed, capped and sent to the I.A.E.A. laboratory for analysis. The sample preparation in the I.A.E.A. laboratory consists of extracting CO_2 from the barium carbonate and synthesizing it with hydrogen gas to methane gas which is the most suitable gas for gas proportional counting. The methane sample was measured in a 0,5-litre volume proportional counter filled up to 5 atmospheres pressure and shielded with an anticoincidence guard counter and lead shield. The main parameters of the counting system were: background 2.8 cpm one sample necessary to obtain sufficiently low statistical error was about and the count rate for "modern" carbon 12.4 cpm. The counting time of 24 hours. A small aliquot of CO_2 gas is measured in a mass spectrometer where the $\frac{^{13}\text{C}}{^{12}\text{C}}$ ratio is compared with that of PDB limestone standard. Tritium analysis is also performed in a gas proportional counter similar to that for ^{14}C measurements. The water sample is quantitatively enriched in tritium by electrolysis and then converted to hydrogen gas. The latter is used to hydrogenate tritium-free ethylene to ethane gas which, in turn, is used for filling the 2.5 litre proportional counter. The tritium counting system parameters were: background 1.0 cpm and efficiency corresponding to 50 T. U./cpm.

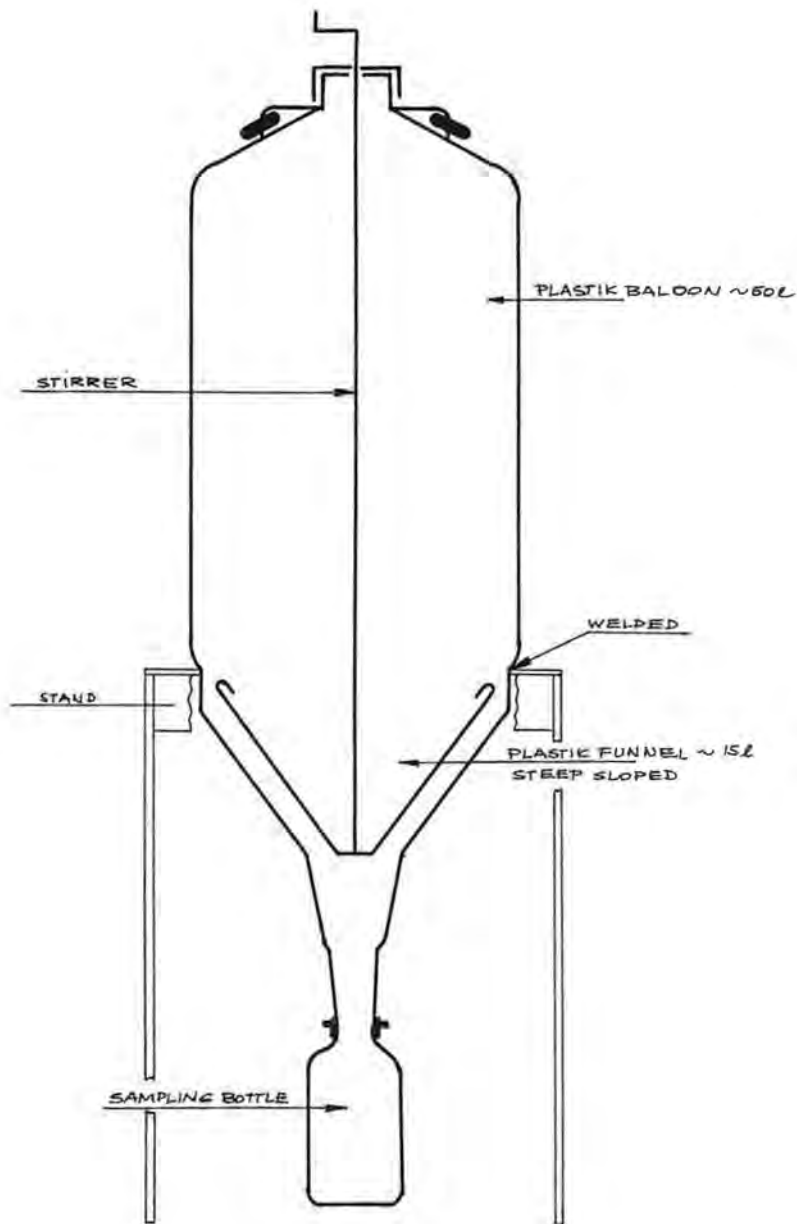


Fig. 1: I.A.E.A. type water sampler for radiocarbon analysis.

The tritium content of the water from the Pyrenees was measured in the Isotope Department of the Bundesversuchs- und Forschungsanstalt Arsenal (Arsenal Federal Research Establishment, under Dr. J. MAIRHOFER). Chemical analysis of the water from Bad Gastein was carried out within two to three days of sampling. The water from the Pyrenees was not analysed until three weeks after sampling and, although there was no observable precipitation during that period, it is likely that the bivalent sulphur concentration was no longer the same as for water fresh from the spring.

Geology

We shall dwell here only briefly on the geological position of the springs in question. In the Bad Gastein region, the granite-gneiss of the Hölltor-Rotgülden "core" swells up to form a cupola which dips below Late Paleozoic and Mesozoic shales at its periphery (CH. EXNER, 1950). Here, within a small area, 21 thermal springs emerge from fissures which have been cut by the Gasteiner Ache (a stream) and which run from the north-north-east with a steep inclination eastwards. In a very similar manner, along the central axis of the Pyrenees warm water frequently emerges around the periphery of granite intrusions—in some cases directly from fissures in the granite and in others from fractures and bedding faults in adjacent metamorphic, Paleozoic formations (C. JOB, 1968).

Bad Gastein Results

Many studies of the chemical composition of Bad Gastein thermal waters have already been carried out by E. KOMMA and F. SCHEMINZKY (1959). Table 1 shows the results of chemical analyses of water from the three springs selected for carbon determination studies. The water from these thermal springs is essentially of the sodium-calcium-sulphate-bicarbonate type mixed to varying extents with surface calcium-bicarbonate water (Fig. 2). The water of the Franz Josef spring (I/23-24) contains about 4800 $\mu\text{val/l}$ dissolved ionized substances. Tritium measurements and chemical analyses both gave a cold surface water content of about 5%. As the infiltrating cold surface water has a lower

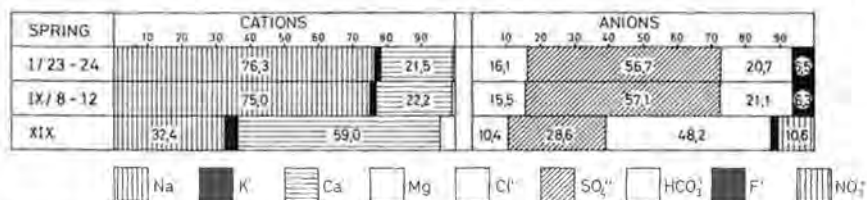


Fig. 2: Relative composition of Bad Gastein thermal waters (in $\mu\text{val}/\%$).

mineral concentration than the rising thermal water, the mineral level of the thermal springs declines with increasing cold surface water concentration. This is clear from the data for the Elisabeth spring (IX/8—12), with a cold surface water concentration of some 12%, and even more so in the case of the Strochner spring (XIX), which cannot be used because of its high cold surface water concentration (80%).

The $\delta^{13}\text{C}$ -values (Table 2) for the carbonates in the water from these springs are slightly lower than the ideal value for vadose water (-12.5%), but come very close to this value. It can, therefore, be assumed with reasonable certainty that biogenic CO_2 played a significant part in the dissolution of the carbonates and that Gastein thermal water is accordingly for the main part infiltrated precipitation.

This result is confirmed by the ^{14}C study. As Table 2 shows, the water from all three springs contains atmospheric ^{14}C . After $\delta^{13}\text{C}$ correction, the ^{14}C concentration in the Strochner spring (XIX) is found to be 195% of the ^{14}C standard. This value corresponds to the current ^{14}C concentration in the atmosphere, which has risen to 200% as a result of nuclear explosions, and is corroborated by the high tritium value of 530 T. U., which indicates that the Strochner spring carries mainly cold surface water. The water from the two other springs (I/23—24 and IX/8—12) contains only about 25% of recent (i. e. before 1950) ^{14}C , corrected by $\delta^{13}\text{C}$ to about 64%, which corresponds to about 3800 years age.

Their ^{14}C content could, of course, also have been raised by infiltration of ^{14}C -rich surface water. However, their tritium values do not move in step with their ^{14}C values: although the tritium concentrations and chemical analyses of springs I/23—24 and IX/8—12 indicate that they carry cold surface water in different proportions (5% and 12% respectively), they have virtually the same ^{14}C concentration.

Assuming that the cold surface water may contain recent ^{14}C concentration (200% of 1950 standard) and its contributions are 5% and 12% to springs I/23—24 and IX/8—12 respectively, the age of the old water component may be calculated by a simple proportion. This would result in about 4700 years and this could be considered as a higher limit for the age of water.

According to EXNER (1950), the catchment area of the Gastein thermal springs is primarily the porphyritic faser granite-gneiss of the Hölltor-Rotgülden "core" which lies to the east of the Graukogel and the Hüttenkogel. The granite-gneiss dips below the shale which covers the western flank of these mountains and re-emerges just in the vicinity of the Gastein thermal springs. On the basis of this geological situation, the nearest infiltration zone would be the depression between the Graukogel and the Hölltorkogel, which is on the average about 3 km from the thermal springs. Taking this distance and the underground flow time of the thermal water, one obtains an infiltration velocity of about

Table 1: Bad Gastein thermal springs: Temperatures of emerging water ($^{\circ}\text{C}$); (pH at 20°); electrolytic conductivity (μS at 20°C); chemical composition ($\mu\text{val/l}$) of the Franz Josef spring (I/23—24), the Elisabeth spring (IX/8—12) and the Stochner spring (XIX). ΣK and ΣA = sum of the cations and anions respectively. Samples were collected on 11 and 12 March 1968.

HOT-SPRING	$^{\circ}\text{C}$	pH	μS	Na^+	K^+	Ca^{++}	Mg^{++}	ΣK	Cl^-	SO_4^{--}	HCO_3^-	F^-	NO_3^-	ΣA	H_2SiO_3 mg/l
I/23—24	45.6	8.1	435	3688	91	1041	16	4836	780	2743	1002	316	0	4841	33.9
IX/8—12	46.6	8.1	415	3493	88	1037	40	4658	719	2648	977	294	1	4639	31.7
XIX	16.1	7.7	257	970	113	1764	145	2992	309	846	1425	62	315	2957	11.4

Table 2: Tritium concentration, $\delta^{13}\text{C}$ -values, ^{14}C content and underground flow time of Bad Gastein thermal waters.

HOT-SPRING	TRITIUM T. U.	$\delta^{13}\text{C}_{\text{‰}}$	$^{14}\text{C}_{\text{‰}}$	$^{14}\text{C}_{\text{‰}}$ corrected	CORRECTED AGE
I/23—24	22.5 ± 1	-10.3	26.1 ± 1.0	63.2	3800 ± 300
IX/8—12	60.0 ± 2	-9.8	25.4 ± 3.0	64.8	3600 ± 1000
XIX	530 ± 20	-11.2	87.3 ± 2.0	195	contemporary

Table 3: Thermal springs in the Pyrenees: Temperatures of emerging water ($^{\circ}\text{C}$); (pH at 20°C); electrolytic conductivity (μS at 20°C); chemical composition (in $\mu\text{val/l}$). ΣK and ΣA = sum of cations and anions respectively. S = bivalent sulphur capable of oxidation to sulphate ($\text{SO}_4^{''}$) — computed as SO_4 . Samples were collected between 24 and 31 July 1968.

HOT-SPRING	$^{\circ}\text{C}$	pH	μS	Na^+	K^+	Ca^{++}	Mg^{++}	ΣK	Cl^-	$\text{SO}_4^{''}$	S	HNO_3	F $^-$	ΣA	H_2SiO_4 mg/l
MOLITG LLUPIA I	35.0	9.2	256	3013	25	64	8	3110	273	302	295	2014	242	3126	42.3
VERNET BARRERA	54.0	9.1	226	2439	51	177	20	2687	218	683	10	1414	316	2641	52.8
THUÉS ANDRÉ	75.0	9.4	243	2802	72	96	0	2970	265	481	261	1561	384	2952	70.1
AMÉLIE FANNY	60.0	9.1	378	4221	136	120	0	4477	675	822	165	2044	821	4527	85.6

Table 4: Tritium concentration, $\delta^{13}\text{C}$ -value, ^{14}C content and underground flow time of thermal waters in the Pyrenees.

HOT-SPRING	TRITIUM T. U.	$\delta^{13}\text{C}\text{‰}$	$^{14}\text{C}\%$	$^{14}\text{C}\%$ corrected	CORRECTED AGE
MOLITG LLUPIA I	1.3 ± 0.3	-16.2	34.0 ± 3.4	52.4	5300 ± 800
VERNET BARRERA	6.4 ± 0.5	-11.9	19.7 ± 2.2	41.4	7300 ± 1100
THUÉS ANDRÉ	2.3 ± 0.3	-12.5	9.1 ± 2.2	18.2	14.000 ± 1700
AMÉLIE FANNY	1.7 ± 0.4	-11.4	5.8 ± 2.3	12.7	17.000 ± 3500

2 mm/day. With such a slow rate of progress, however, one would have to assume the existence of an extensive network of large fissures covering an area of 2 km² in order to explain the total discharge of about 4500 m³/day from the Gastein springs.

Results for the Pyrenees

On the whole, the thermal waters of the Pyrenees have a lower mineral concentration than those of Bad Gastein (Table 3). Their dissolved mineral content lies in the range 2700—3100 $\mu\text{val}/\text{l}$. Only the Fanny spring of Amélie, with about 4500 $\mu\text{val}/\text{l}$, approaches the degree of mineralization of Gastein thermal water. Fig. 3 shows that, as in Gastein, sodium ions predominate on the cation side, while the anions

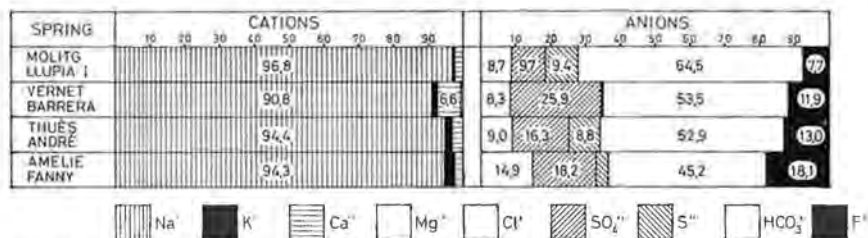


Fig. 3: Relative composition of Pyrenean thermal waters (in $\mu\text{val } \%$).

comprise chlorides, sulphates, bicarbonates and fluorides; however, the percentage distribution of the latter differs somewhat from that found in Gastein. In addition, almost all Pyrenean thermal waters contain bivalent sulphur, which is virtually absent from Gastein thermal water. A noteworthy feature of the Pyrenean waters is their high fluorine content. The springs of Molitg, Thuès and Amélie are sodium-bicarbonate-sulphur springs, while the Vernet spring is a sodium-bicarbonate-sulphate spring. Like Gastein thermal water, all Pyrenean thermal waters contain more silicic acid and silicates in solution (34—86 mg/l — Tables 1 and 3) than appear to be present in normal surface waters (2—8 mg/l). As the low tritium values show (Table 3), the infiltration of cold surface water is insignificant in the case of the Pyrenean thermal springs.

The $\delta^{13}\text{C}$ -values lie between — 16.2‰ and — 11.4‰, again not too far from the ideal value for vadose water (— 12.5‰). In other words, the Pyrenean thermal springs, too, carry mainly vadose water. The corrected ¹⁴C values give underground flow times of between 5300 and 17 000 years. As nothing is known about the location of the catchment areas, it is impossible to estimate the infiltration velocity.

Silicate and Fluorine Concentrations in Relation to the Age of the Waters Estimated from ^{14}C Data

Comparing the underground flow times of the Bad Gastein and Pyrenean thermal waters with the results of the chemical analyses, we find a remarkable correlation between age, estimated from ^{14}C data and dissolved silicic acid and silicate concentration (Fig. 4). The correlation coefficient r is 0.98, a value which—in spite of the small number of samples—is 99.9% certain. There is an almost equally strong dependence on the relative fluorine content ($r = 0.96$). At present, only tentative conclusions can be drawn regarding the significance of these correlations. The hot thermal waters of recent volcanic regions (New Zealand, Iceland, North America) contain in most cases considerable amounts of silicate and fluorsilicate, which upon cooling are deposited in the form of huge terraces of siliceous sinter around the spring (A. RITTMANN, 1960). Since the solubility of silicates increases with rising temperature, the silicate concentration could move in step with the

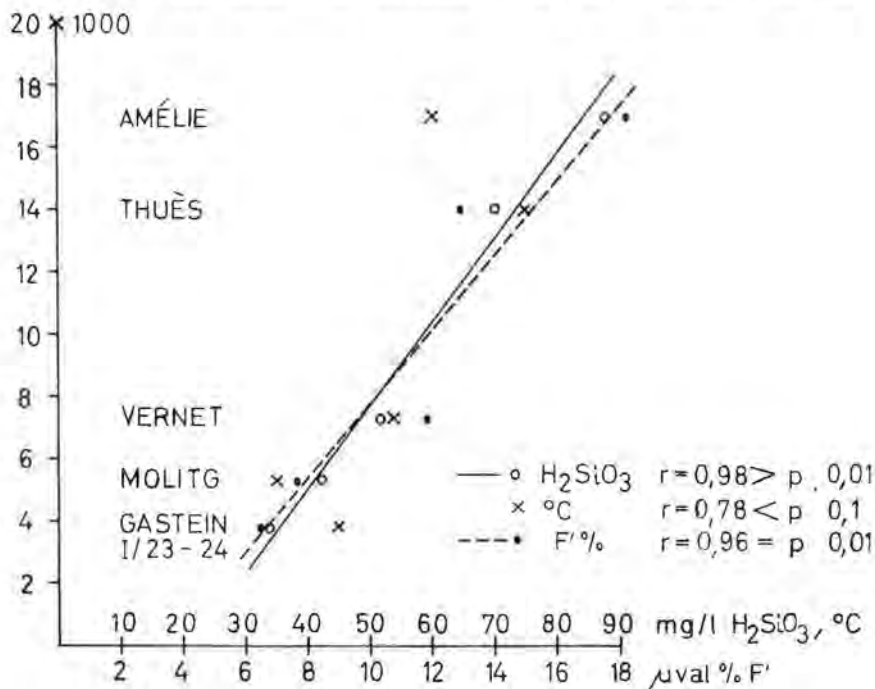


Fig. 4: Correlation of ^{14}C -estimated age (in years, along the ordinate) with dissolved silicate concentration (circles) and with relative fluorine content (points) for Bad Gastein and Pyrenean thermal waters. There is no certain correlation with the temperature of the emerging water (crosses).

temperature of the spring water. This seems to be contradicted by the fact that the temperatures of the waters emerging from the springs which we studied are not significantly correlated with the underground flow time (Fig. 4). However, it should be borne in mind that, particularly if the discharge rate of the spring is low, thermal waters often cool down only during the last few metres before emerging, so that the silicate content is perhaps a better indicator of the temperature at low levels than the temperature of the emerging water. If this rather daring hypothesis is provisionally accepted, it follows that, the higher their temperatures, the greater is the age of the thermal waters. This could have two quite different causes: first, that the infiltrating precipitation undergoes greater heating and spends longer underground if it infiltrates deeper; or else, that as a result of isotopic exchange, which increases with rising temperature, the water appears to be older the hotter it has become.

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Zusammenfassung

Die C-Isotopen- und Tritiumuntersuchungen wurden an zwei Thermalwässern und einem Mischwasser in Badgastein (März 1968) sowie an vier Thermalwässern in den Pyrenäen (Juli 1968) durchgeführt.

Über die chemische Zusammensetzung der Thermalwässer von Badgastein gibt es bereits zahlreiche Untersuchungen. Die chemischen Analysen der drei für die C-Isotopenbestimmung ausgewählten Quellen zeigt Tab. 1. Im wesentlichen handelt es sich um Thermalwässer des Na-, Ca-, Sulfat-, Hydrogenkarbonattyps, die mehr oder weniger mit oberflächlichem Calcium-Hydrogenkarbonat-Wasser vermischt sind. Der Gehalt an gelösten ionisierten Stoffen beträgt im Wasser der Franz-Josef-Quelle (I/23—24) rund 4800 $\mu\text{val/l}$. Tritiummessungen und chemische Analysen ergaben übereinstimmend einen Kaltwasseranteil von ca. 5%. Da die zuzusätzlichen Kaltwässer schwächer mineralisiert sind als das aus der Tiefe aufsteigende Thermalwasser, nimmt die Mineralisierung ab, je größer der Kaltwasseranteil der Thermalquellen ist. Dies zeigt sich z. B. bei der Elisabethquelle (IX/8—12), die etwa 12% Kaltwasser führt, und wird besonders deutlich bei der wegen ihres hohen (60 bis 80%) Kaltwasseranteils nicht nutzbaren Strochnerquelle (XIX).

Die $\delta^{13}\text{C}$ -Werte der Karbonate dieser Quellwässer liegen etwas unterhalb des für vadose Wässer im Idealfall zu erwartenden Wertes von $-12,5\%$, kommen aber recht nahe an diesen Wert heran. Daher kann mit ziemlicher Sicherheit angenommen werden, daß biogenes CO_2 an der Auflösung der Karbonate maßgeblich beteiligt war und daß daher das Gasteiner Thermalwasser überwiegend versickertes Niederschlagswasser ist.

Dieses Resultat wird durch die ^{14}C -Untersuchung bestätigt. Aus den korrigierten ^{14}C -Gehalten ergibt sich für das Gasteiner Thermalwasser eine unterirdische Laufzeit von 3600 bis 3800 Jahren.

Die Thermalwässer der Pyrenäen sind im allgemeinen schwächer mineralisiert als das Thermalwasser von Badgastein. Ihr Gehalt an gelösten mineralisierten Stoffen liegt zwischen 2700 und 3100 $\mu\text{val/l}$. Nur die Fanny-Quelle von Amélie erreicht mit rund 4500 $\mu\text{val/l}$ beinahe den Mineralisierungsgrad des Gasteiner Thermalwassers. Die chemische Charakteristik der Pyrenäethermen zeigt auf der Kationenseite — ähnlich wie in Gastein — ein Überwiegen der Na-Ionen, auf der Anionenseite finden sich Chloride, Sulfate, Hydrogenkarbonate und Fluoride, deren prozentuelle Verteilung jedoch etwas von der des Gasteiner Thermalwassers abweicht. Außerdem enthalten fast alle Pyrenäethermen zweiwertigen Schwefel, der im Gasteiner Thermalwasser praktisch fehlt. Bemerkenswert ist der hohe Fluorgehalt der Pyrenäenwässer. Die Quellen von Mollitg, Thuès und Amélie sind Na-Hydrogenkarbonat-Schwefel-Thermen, die Quelle von Vernet ist eine Na-Hydrogenkarbonat-Sulfat-Therme. Alle Thermalwässer der Pyrenäen enthalten wie das Gasteiner Thermalwasser mehr Kieselsäure und Silikate gelöst (34 bis 86 mg/l), als nach bisherigen Erfahrungen in gewöhnlichen Oberflächenwässern vorkommen (2 bis 8 mg/l). Die Kaltwasserinfiltration ist in den Pyrenäethermen, wie die niedrigen Tritiumwerte zeigen, unbedeutend.

Die $\delta^{13}\text{C}$ -Werte liegen zwischen $-16,2$ und $-11,4\%$, also wiederum nicht allzuweit entfernt vom Idealwert vadoser Wässer ($-12,5\%$), das

heißt, auch die Pyrenäethermen führen überwiegend vadoses Niederschlagswasser. Die korrigierten ^{14}C -Werte ergeben unterirdische Laufzeiten zwischen 5300 und 17.000 Jahren.

Beim Vergleich der unterirdischen Laufzeiten der Thermalwässer von Badgastein und aus den Pyrenäen mit den chemischen Analysen fällt eine bemerkenswerte Korrelation zwischen ihrem Gehalt an gelöster Kieselsäure und Silikaten und dem ^{14}C -Alter der Wässer auf (Abb. 4). Der Korrelationskoeffizient r beträgt 0,98 und ist trotz der kleinen Probenzahl mit 99,9% gegen 0 gesichert. Eine nahezu gleich starke Abhängigkeit besteht auch zum relativen Fluorgehalt der Wässer ($r = 0,96$). Über die Bedeutung dieser Beziehungen lassen sich vorläufig nur Vermutungen anstellen.

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